

Superior Decomposition of NO over Plasma-Assisted Catalytic System Induced by Microwave

Hyun-Seog Roh, Yong-Ki Park, and Sang-Eon Park*

Catalysis Center for Molecular Engineering, Korea Research Institute of Chemical Technology (KRICT), Taejeon 305-600, Korea

(Received February 14, 2000; CL-000153)

More than 99% of NO was directly decomposed into N₂ and O₂ without formation of N₂O at space velocity of 45360 h⁻¹ and apparent temperature of 280 °C over plasma-assisted Co₃O₄/Cu-ZSM-5 catalyst.

Nitrogen oxides in exhaust gases are major sources of air pollution, and new abatement technologies are being developed to overcome current NH₃-SCR or SNCR. Direct decomposition of NO has been proposed as one of candidates for NO_x abatement. Since Iwamoto et al. pioneered direct decomposition of NO over Cu-exchanged zeolite catalyst,^{1,2} other types of zeolites or mixed metal oxides have been suggested but their catalytic performances are still too low to satisfy practical application. As an alternative for the decomposition of NO, plasma could be considered induced by microwave or electrical discharge. However, due to the difficulties in generating and controlling the quality at atmospheric condition, its application also has been limited. That is, high electric field energy at atmospheric condition or microwave at low pressure are required for its generation.^{3,4} To circumvent limit of plasma itself for the abatement of NO_x, several types of plasma processes combined with catalysts or reductants have been proposed. These were effective for the decomposition of NO_x at atmospheric pressure and low-temperature but their activities decreased rapidly at high space velocity (> 5000 h⁻¹).^{4,5} So, we tried to overcome the limits exposed in plasma-assisted NO decomposition by reinforcing catalytic function to the plasma. It was successful and superior NO decomposition activity was obtained over this plasma-assisted catalytic system even at high space velocity.

The catalysts were designed to introduce functions of NO decomposition and microwave absorbing for plasma generation. As a microwave absorbent, two types of dielectric materials having high microwave loss factor were chosen; one is catalytically inert SiC and the other is Co₃O₄ having NO decomposition activity. These microwave absorbents were dispersed combinatorially on two types of porous supports using impregnation method; one is catalytically inert silica and the other is Cu-ZSM-5 having high NO decomposition activity. Cu-ZSM-5 was prepared by ion-exchange method. All catalysts were dried and calcined at 120 °C for 2 h and 550 °C for 6 h. These four types of catalysts could be heated up to 1000 °C by increasing the loading of microwave absorbents. To reach 500 °C for plasma generation, 25 wt% of Co₃O₄ and 95 wt% of SiC were required in 300 W microwave input power, respectively. Prior to plasma generation the catalysts were treated in He flow at 150 °C for 1 h. Plasma was triggered by controlling input power of microwave in He flow. The input power was increased gradually up to 300 W/g-cat. to reach 500 °C. At a certain point around this temperature, reflected microwave power dropped rapidly to almost zero and light blue-colored plasma was formed (Table 1). Stable and blue-colored plasma was obtained

Table 1. NO decomposition over various plasma-assisted catalytic systems induced by microwave (GHSV = 45360 h⁻¹, Input microwave power = 100 W).

Microwave Absorbent	Support	NO Conv. /%	Temp. /°C	Reflected Power /W
SiC	Silica ^a (5wt%)	0.1	238	16
SiC	Cu/ZSM-5 ^b (5wt%)	95.1	312	5
Co ₃ O ₄	Silica ^a (75wt%)	97.0	286	3
Co ₃ O ₄	Cu/ZSM-5 ^b (75wt%)	99.4	280	3

^aSurface area = 400 m²/g, Pore dia. = 300 Å, Pore vol. = 3.0 ml/g (PQ corp., MS-3040). ^bDegree of Cu ion-exchange = 100% Si/Al = 15, Surface area = 425 m²/g (PQ, CBV 3020E).

over all of the prepared catalysts by the irradiation of continuous microwave in atmospheric condition without vacuum. However, the quality of plasma was strongly influenced by the loading of microwave absorbents. At lower loading, the microwave could not be absorbed enough to trigger plasma while at too high loading most of the absorbed microwave energy was dissipated as radiation heat instead of plasma generation due to the enhanced heating (> 600 °C). Thus, to utilize microwave effectively for NO decomposition, the loading should be controlled strictly in the region of plasma formation. To see the catalytic functions of plasma-assisted catalytic system, NO decomposition was carried out in a microwave reaction apparatus similar to Wan et al.'s⁶ equipped with specially designed fixed-bed quartz reactor and 2.45 GHz microwave generator (ASTEX, Model AX 3120) (Table 1). NO decomposition was carried out in the plasma-catalytic reaction system while changing NO concentration from 1000 to 10000 ppm NO/He and flow rate from 120 to 1200 ml/min over 1g catalyst. The quartz reactor was specifically designed to locate catalyst cylindrically inside of the reactor for uniform microwave absorbing and heat distribution. That is, because the microwave is mainly absorbed by the catalyst located outer part of reactor the inner part of quartz reactor was blanked such as empty torus. Products were monitored by a chemiluminescent NO_x analyzer (42H, Thermo. Env. Inc.) and GC (HP-5890) equipped with molecular sieve 13X column. Temperature was measured by IR pyrothermometer (MIKRON M90-ZB).

For all of the catalysts, plasma was indispensable to achieve high decomposition activity. The catalysts unable to produce plasma did not show any activity even though the apparent temperature was higher than 500 °C. The catalytically inert SiC/silica did not show any decomposition activity even in the presence of stable blue-colored plasma. However, 5 wt% Cu-ZSM-5 loaded on SiC showed 95% NO conversion at 45360 h⁻¹. The decomposed NO was converted into N₂ and O₂ without detectable formation of N₂O. This superior decomposition activity over SiC/Cu-ZSM-5 may be resulted from the cat-

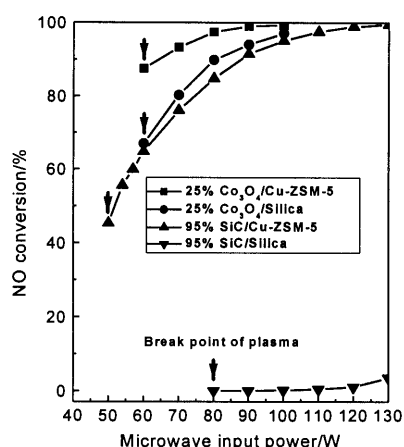
Table 2. Comparison of NO decomposition activity depending on reaction types.

Reaction type	Catalyst	GHSV /h ⁻¹	NO Conc. /ppm	Conv. /%	Temp. /°C
Plasma-catalytic ^a (Microwave)	Co ₃ O ₄ / Cu-ZSM-5	4536	1000	99.4	279
		4536	10000	95.0	277
		45360	1000	97.8	267
Catalytic ²	Cu-ZSM-5 ^b	375	10000	100	480
		7500		40–60	
Plasma ⁴ (AC 4.2 kV)	–	3000	10000	80	–
		9000		44	
		18000		21	

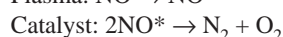
^aInput power of microwave (P_{in}) = 80 W. ^bDegree of Cu ion-exchange = 122%, Si/Al = 23.3.

alytic function of Cu-ZSM-5 assisted by plasma. It is a good contrast to the AC, DC or Corona discharge plasma systems where only limited conversion and selectivity were obtained at high space velocity.⁴ Contrast to the SiC, the Co₃O₄ showed quite different behavior as a microwave absorbent. It has high decomposition activity itself as well as microwave absorbing ability and NO could be decomposed effectively without the help of NO decomposition catalyst. The Co₃O₄ has high NO sorption ability as one of main component in NO decomposition catalyst,^{7,8} which may be the reason for high activity in plasma-assisted NO decomposition. When the Co₃O₄ was modified further with catalytically active Cu-ZSM-5 (75 wt%), it was strengthened enough to decompose NO at space velocity higher than 45000 h⁻¹ (Table 2). This improved catalytic performance was not observed in other combination of microwave absorbents and supports, which makes it clear that both plasma and catalytic function are necessary for superior decomposition activity of NO. To clarify the importance of catalyst in plasma-assisted catalytic system, decomposition activities of this study were compared with those of pure plasma and catalyst itself (Table 2). In our system, we changed the Cu ion-exchange level from 100 % to 122 %, and Si/Al ratio from 15 to 40, but there was not any significant change. Different from the plasma-assisted catalytic system, the decomposition activities are strongly influenced by the space velocity in catalytic or plasma reactions. At the space velocity higher than 10000 h⁻¹, conversion decreased to the half of their initial activity. In the case of AC plasma, even high input voltage of 2.75 kV is applied it is impossible to decomposed more than 20% of NO at 18000 h⁻¹. However, the limits exposed in catalytic or plasma systems could be overcome easily in our plasma-assisted catalytic system induced by microwave. More than 95% of conversion of NO was achieved even at 45360 h⁻¹, which is superior to the catalyst or plasma itself.

The dependence of microwave power was also checked in decomposition activity (Figure 1). According to the types of catalysts, decomposition activities showed different behaviors. In the case of catalytically reinforced Co₃O₄/Cu-ZSM-5, activity was maintained constantly regardless of input microwave power until the plasma broke down. However, in other catalyst activities decreased as the input power decreased. This means that both plasma and catalytic function are important but the catalytic function is more important than plasma. Once the plas-

**Figure 1.** NO decomposition activity vs. microwave input power in plasma-catalytic reaction induced by microwave (1 g catalyst, 1000 ppm NO in He balance, and GHSV = 45360 h⁻¹).

ma is formed then it can provide enough energy to the NO molecules to be activated to the transition state and the activated NO molecules will recombine into NO again or decompose into N₂ and O₂. In pure plasma system, this process will strongly depend on the probability of collisions and only limited amounts of NO will decompose. However, by locating decomposition catalyst in the plasma, the recombination process will be influenced through the preferential interaction of activated NO molecules with catalyst. That is, the decay of activated NO will convert catalytically into thermodynamically stable N₂ and O₂ through selective recombination of N-N and O-O bonds over decomposition catalyst proposed as follows. Co and Cu species could be suggested as active sites for NO decomposition. However, it is a suggestion and further spectroscopy study should be done to verify it more clearly.



In conclusion, plasma-assisted Co₃O₄/Cu-ZSM-5 catalyst shows remarkably high activity (99%) for the direct decomposition of NO into N₂ and O₂ at GHSV > 45000 h⁻¹ and apparent temperature of 280 °C.

References

- 1 M. Iwamoto, S. Yokoo, K. Sakai, and S. Kagawa, *J. Chem. Soc., Faraday Trans. 1*, **77**, 1629 (1981).
- 2 M. Iwamoto, H. Yahiro, K. Tanda, N. Mizuno, Y. Mine, and S. Kagawa, *J. Phys. Chem.*, **95**, 3727 (1991).
- 3 J. Huang and S.L. Suib, *J. Phys. Chem.*, **97**, 9403 (1993).
- 4 J. Luo, S.L. Suib, M. Marquez, Y. Hayashi, and H. Matsumoto, *J. Phys. Chem. A*, **102**, 7954 (1998).
- 5 H. Miessner, R. Rudolph, and K.-P. Francke, *Chem. Commun.*, **1998**, 2725.
- 6 J. K. S. Wan, G. Bamwenda, and M. C. Depew, *Res. Chem. Intermed.*, **16**, 241 (1991).
- 7 J. W. Hightower and D. A. Leisburg, "Current Status of the Catalytic Decomposition of NO," ed by R. L. Klimisch and J. G. Larson, Plenum Press, New York-London (1975).
- 8 D. Klvana, J. Kirchnerova, and C. Tofan, *Korean J. Chem. Eng.*, **16**, 440 (1999).